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(54) Title: PROCESS FOR THE CONVERSION OF POLYSULFANES

(57) Abstract: The invention provides a process for the removal of polysulfanes from gas streams formed during H₂S synthesis.

Process for the Conversion of Polysulfanes

Field of the Invention

The invention relates to a process for the removal of polysulfanes from gas streams formed during H_2S synthesis.

5 Background

In H_2S syntheses from hydrogen and sulfur, polysulfanes (H_2S_n) are generally found as by-products in the crude gas in an order of magnitude of ≥ 400 vpm (volume per million), and when the gas stream is compressed these tend
10 to decompose in an uncontrolled manner into H_2S and sulfur. This leads to undesirable sulfur deposits in the whole of the compression area, including the peripheral pipes and valves.

It is known that polysulfanes are thermodynamically
15 unstable and have a tendency to decompose, particularly when heated (M. Schmidt, W. Siebert: "Sulfane" in Comprehensive Inorganic Chemistry, vol. 2, sect. 2.1, Pergamon Press, Oxford 1973, 826-842).

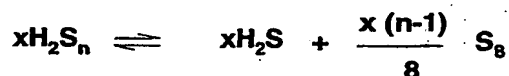
Traces of alkali on the surface of glass vessels lead to
20 the deposition of elemental sulfur.

However, these findings come from investigations with polysulfanes present in more or less pure form.

In principle, of course, they also apply to polysulfanes present in great dilution.

25 In this case, however, the influence of the concentration ratios has to be taken into account.

Under the above circumstances, the polysulfanes are present in great dilution in hydrogen sulfide, which at the same time represents a decomposition product of the
30 polysulfanes in a thermodynamic equilibrium:



The high H_2S concentration makes the shift of the equilibrium to the left-hand side seem probable and the decomposition of the polysulfanes into hydrogen sulfide and sulfur to be a non-preferred reaction.

The object of the invention is to provide a process for the practically complete removal of the polysulfanes, thus preventing sulfur deposits in the plant's pipes.

10 Summary of the Invention

The invention provides a process for the removal of polysulfanes from crude gas formed during the production of hydrogen sulfide, characterized in that the crude gas, with a content of > 80 vol., preferably > 95 vol. H_2S and > 100 to 2000 vpm, particularly > 400 to 1500 vpm, of polysulfanes (H_2S_n with $n: 2$ to 8), is passed through an optionally multi-stage washer system, brought into contact with water and/or methanol, preferably with basic aqueous and/or methanol systems, and a pure gas is obtained in which the polysulfanes are present depleted by > 50 to $> 99.5\%$, based on the starting value.

The quantities of polysulfanes can optionally also be more than 2000 vpm.

Detailed Description of the Invention

25 Jet washers are preferably used, which, like other washers, can be operated at a pressure of 1.05 to 10 bara, preferably at 1.05 to 2 bara.

Unpressurized operation is an alternative, however. In particular, aqueous and/or methanolic 0.5 to 20 wt.%, preferably 0.5 to 10 wt.%, solutions of alkali hydroxides

or oxides, especially KOH/KHS or NaOH/NaHS solutions, are used as washing fluid.

The hydrogen sulfides are formed while passing the gas streams through the washing fluid.

- 5 Appropriately concentrated solutions of other basic oxides or hydroxides, especially of alkaline earth hydroxides or oxides, preferably those of calcium, can also be used.

The polysulfanes are also removed from the gas streams by basic aqueous and/or methanolic 1 - 20%, preferably 1 to 10 wt.%, solutions of ammonia, organic amines, of the general formula $(C_nH_{2n+1})_xNH_y$ with $n=1, 2, 3$; $x=2, 3$; $y=0, 1$ or amino alcohols of the general formula $(C_nH_{2n+1}O)_xNH_y$ with $n=1, 2, 3$; $x=2, 3$; $y=0, 1$.

15 The suitable temperature range is generally between 0 and 150°C, especially 10 and 60°C.

At gas velocities of the crude gas to be purified of generally between 0.1 and 25 m/s, especially 10 and 22 m/s, the polysulfanes are removed from the gas streams with a degree of depletion of > 50 to > 99.5%, preferably > 70 to > 99.5%, based on the starting content in the crude gas.

For a content of > 500 vpm in the crude gas, this corresponds to a depletion to < 10 vpm in the pure gas.

25 The sulfur formed during the conversion of the polysulfanes goes into solution, among other things as a result of the formation of the corresponding polysulfides. Sulfur precipitated in solid form can optionally be discharged with the aid of suitable filtration devices. The washing solution circulates and is discharged as a function of the polysulfide/sulfur load. The washing fluid is topped up as a function of the rate of discharge and of quantities of solvent that may evaporate. To remove any

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residual quantities of polysulfanes present after the jet washer (generally $\leq 20\%$ of the starting quantity), the H_2S -containing gas is generally after-treated with the above-mentioned solutions in a washing column or a packed bed in counter-current (counter-current washer). Entrained droplets are separated by means of a demister system. Any quantities of sulfane remaining in the gas stream of purified H_2S can also be broken down in a downstream adsorber bed (activated carbon, zeolite) and the sulfur formed can be separated off.

Analytical

The analytical acquisition of the sulfane concentration in the crude and pure gas takes place by means of an online UV measurement. Parallel to this, sulfur contents in the washing solution and sulfane and sulfur concentration in the H_2S -containing gas stream are determined by wet-chemical means as required.

With the aid of the process according to the invention, it is possible to deplete the polysulfanes to such an extent that, in downstream processes, e.g. compressor stages, undesirable sulfur deposits are avoided..

Examples

Crude gases with a polysulfane content of > 400 to 2000 vpm are used.

The polysulfane concentrations are dependent upon the reaction conditions in the H_2S reactor.

Comparative Example 1

H_2S crude gas was passed through an adsorption column packed with approx. 7 l of etched Raschig rings at 20 Nm³/h. The sulfur forming by decomposition of the polysulfanes was deposited on the surface of the packings.

A degree of depletion of 25% was achieved. Service life of the adsorber bed 20 h.

Comparative Example 2

H₂S crude gas was passed through an adsorption column
5 packed with approx. 7 l of SiO₂ supports (particle size 3 - 5 mm) at 20 Nm³/h. The sulfur forming by decomposition of the polysulfanes was deposited on the surface of the packings. A degree of depletion of 50% was achieved. Service life of the adsorber bed 48 h.

10 Example 1

H₂S crude gas was passed first through a jet washer system operated only with water and then through an adsorption column packed with approx. 12 l of activated carbon (particle size 5 - 6 mm) at 200 Nm³/h for 60 h. Before
15 entering the adsorption column, a degree of depletion of 75% and after the column a value of > 99% was measured.

Example 2

H₂S crude gas was passed first through a jet washer system supplied with methanol at 200 Nm³/h for 48 h. A degree of
20 depletion of > 50% was achieved, based on the crude gas.

Example 3

H₂S crude gas was passed first through a washing column operated with a methanol/triethanolamine mixture (5% triethanolamine) for 24 h at 10 Nm³/h. The sulfur forming
25 as a result of decomposition of polysulfanes dissolved in the washing solution. A degree of depletion of 80% was achieved.

Example 4

H₂S crude gas was passed through a jet washer system supplied with a methanol/NaOH mixture (5% NaOH) for 400 h at 200 Nm³/h. A degree of depletion of 99% was achieved.

5 The sulfur deposited after a running time of approx. 200 h was removed from the washer circulation with the aid of in-line filtration.

Example 5

10 H₂S crude gas was passed through a jet washer system supplied with a water/KOH mixture (12% KOH) for 200 h at 200 Nm³/h. A degree of depletion of 99.5% was achieved.

What is claimed is:

1. Process for the removal of polysulfanes from crude gas formed during the production of hydrogen sulfide, characterized in that the crude gas, with a content of > 80 vol.% H_2S and > 100 to 2000 vpm, especially > 400 to 1500 vpm polysulfanes (H_2S_n with $n: 2$ to 8), is passed through a washer system, brought into contact there with water and/or methanol and a pure gas is obtained.
2. Process according to claim 1, characterized in that a 0.5 to 20 wt.% aqueous and/or methanolic solutions of an alkali or alkaline earth hydroxide or oxide is used as washing fluid.
3. Process according to claim 1, characterized in that 1 to 20 wt.% aqueous and/or methanolic solutions of organic amines of the general formula $(C_nH_{2n+1})_xNH_y$ with $n=1,2,3$; $x=2,3$; $y=0,1$; amino alcohols of the general formula $(C_nH_{2n+1}O)_xNH_y$ with $n=1,2,3$; $x=2,3$; $y=0,1$ or ammonia are used as washing fluid.
4. Process according to one or more of claims 1 to 3, characterized in that a jet washer is used.
5. Process according to claims 1 to 4, characterized in that the pre-purified gas is after-treated in a counter-current washer with aqueous or methanolic solutions.
6. Process according to claims 1 to 4, characterized in that the gas depleted in polysulfanes is passed through an adsorber bed.
7. Process according to one or more of claims 1 to 6, characterized in that the polysulfanes contained in the crude gas are depleted in the pure gas at a rate of > 50 to $> 99.5\%$, based on the crude gas.

8. Process according to one or more of claims 1 to 7, characterized in that the process is carried out at a temperature of 0 to 150°C.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/09432

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B17/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 17 68 826 B (DEGUSSA) 26 August 1971 (1971-08-26) column 3, line 6 - line 31; claims; figure	1-8
A	US 2 479 781 A (ROBINSON SAM P) 23 August 1949 (1949-08-23)	
A	US 2 784 055 A (LEONARD SILVER) 5 March 1957 (1957-03-05)	
A	US 5 866 721 A (GOEDECKE RALF ET AL) 2 February 1999 (1999-02-02)	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/EP 03/09432

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